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XXIX.—*On the Production of a Blue Substance by the Electrolysis of Sulphate of Aniline.*

By H. Letheby, M.B., M.A., Ph.D., &c.

[Professor of Chemistry in the College of the London Hospital.]

Having had to investigate two cases of fatal poisoning by nitrobenzol, and finding that this compound is changed in the living stomach into aniline, I was led to enquire into the chemical reactions of this alkali, in the hope of discovering a delicate and certain test for it. That which first commanded my attention was the fact, that a salt of aniline, under the influence of nascent oxygen, from any source, acquired a blue or purple colour. But the reactions were not in all cases equally delicate, a $\frac{1}{1000}$ of a grain of aniline in half a drop of dilute sulphuric acid (1 to 1) gradually became blue when treated with a little peroxide of lead, or red prussiate of potash, but it required about double this quantity of aniline to show the blue or purple reaction with peroxide of manganese or bichromate of potash; and it was hardly possible to bring out the distinctive colours with less than the $\frac{1}{100}$ part of a grain, with peroxide of hydrogen, peroxide of barium, chlorine or chloride of lime. Referring to my original experiments with strychnine, in which I found that a sulphatic solution of the alkaloid was instantly coloured deep blue, when placed upon a strip of platinum and brought under the influence of the nascent oxygen from the positive pole of a galvanic battery, it occurred to me that the same mode of manipulation with aniline would be attended with a like result. I therefore took a little of the alkali and dissolved it in dilute sulphuric acid (about 1 to 1), and placed a single drop of the solution on a strip of platinum; the platinum was brought into contact with the positive pole of a small Grove's battery (3 inches by 2), and the solution was touched with the negative pole. Instantly the liquid acquired a purple and finally a pinkish colour. This

reaction was distinct and very fully characteristic when only the $\frac{1}{2000}$ of a grain of aniline was used. It was, therefore, by far the most delicate of all the nascent oxygen tests for the alkali.

In the course of my medico-legal enquiries, however, I found that, with strong solutions of the alkali, the colour was not violet but deep blue, and sometimes greenish blue, and that the pigment adhered as a fine powder to the platinum. It occurred to me, therefore, that it would be interesting to procure this pigment in a somewhat large quantity in order that its nature might be ascertained. About two ounces of aniline were dissolved in dilute sulphuric acid, and placed in a large beaker. It was then brought under the electrolytic action of two sets of Grove's batteries (each 6 inches by 4) arranged for intensity. A sheet of platinum 6 inches by 4 was placed in the aniline solution and brought into contact with the positive pole of the battery, a flat porous cell containing dilute sulphuric acid was also placed in the solution, and this was connected by a similar sheet of platinum with the negative pole of the battery. By this arrangement, the nascent hydrogen from the negative pole was kept apart from the aniline solution, so that the nascent oxygen from the positive pole might have free and undisturbed action on the aniline. Very soon the positive sheet of platinum became covered with a thick layer of dirty bluish-green pigment. This was removed, and, after being well washed with water, was collected in a filter and dried. Its leading properties are as follows :—

It occurs in the form of a dirty bluish-black powder, which is insoluble in water, alcohol, ether, ammonia, &c. While it rests on the platinum, it acquires a brilliant blue colour by immersion in ammonia, but the blue pigment does not dissolve.

Concentrated sulphuric acid dissolves it, and forms a blue, a green, or a violet solution according to the degree of concentration; and when the solution is diluted with water, a dirty emerald green powder subsides. This is also made blue by concentrated ammonia, and blue or purple by concentrated sulphuric acid.

The blue pigment is partly decolorized by reducing agents, or lime and sulphate of iron; and in this condition it dissolves, and, like indigo, acquires a blue colour on exposure to the air.

The dry pigment is decomposed at a red heat, evolving water and sulphurous acid, and leaving a black cinder.

The composition and chemical reactions of the pigment are now being investigated by Mr. Fewtrell and myself, and will be here-

after the subject of communication to the Society. The present note is merely intended as an exposition of the fact, that a blue pigment is produced by the electrolytic oxidation of a sulphatic solution of aniline.

XXX.—*On the Properties of Liquid Carbonic Acid.*

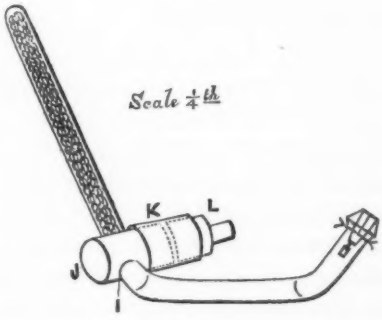
By George Gore, Esq.

[Abstracted from the Philosopical Transactions, 1861, Part i.]

1. A stout glass tube, of the form shewn in Fig. 1, was filled in its distant limb with small pieces of sesqui-carbonate of ammonia, the last pieces of which were pushed in firmly by means of a rod of gutta-percha; the horizontal part was then filled with strong sulphuric acid. A small cup of glass, containing the substance to be submitted to the action of the carbonic acid, was fixed by heat upon the inner end of the gutta-percha stopper; the stopper wetted with a saturated solution of paraffin in chloroform, then forced strongly (with caution) into the mouth of the tube, and secured firmly by transvere binding wire.

2. For convenience of manipulation, the tube was placed in the hole of a transversely perforated cork; the cork fitted rather loosely in a short piece of brass tube; the tube fixed upon a wooden peg, as shown in figure 1, in which I is the hole, J the Cork, K the brass tube, and L the wooden peg with a prolongation of smaller diameter. The cork could thus be readily turned upon its axis, and the glass tube placed and retained in various positions.

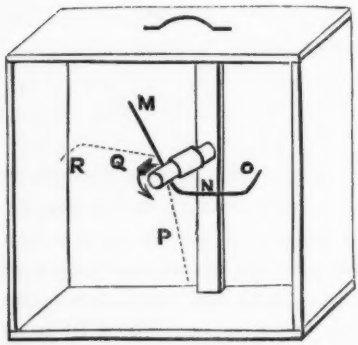
Fig. 1.



3. As a protection from accidents by explosion, and for further convenience of manipulation, a moveable cage or box was con-

structed for each tube; its sides. top, and bottom were made of wood, and its front and back were of fine iron wire-gauze; its dimensions were 12 inches high, 12 inches wide, and 5 inches from front to back; the pieces of gauze were nailed to the wood on one of their vertical edges only, so that they served the purpose of doors. A small vertical strip or piece of wood was fixed at the back part of the box, with a hole at its middle part to receive tightly the small projecting part of the horizontal L, fig. 4. An inspection of fig. 2 will make more clear the whole arrangement.

Fig. 2.



4. The tube, charged with its acid and carbonate, is placed in the frame in the position shown by the lines M, N, O in fig. 2; and the operator having previously protected his hands by thick leather gloves, his eyes by a pair of spectacles, and keeping the wire-gauze door between his face and the tube, occasionally turns the supporting cork upon its axis in the direction of the arrow, so as to cause a little of the acid to flow upon the alkaline carbonate; this must be done with cautious watching and in very small quantities at the commencement, otherwise the bubbles of gas which ascend through the oil of vitriol will carry some of the latter acid into contact with the contents of the little glass cup. The process requires much watching, and if at any time the chemical action is allowed to progress too rapidly, the generating tube is liable to burst in consequence of the heat evolved.

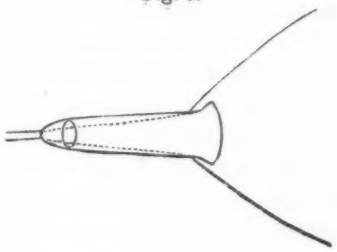
5. The tube is thus occasionally turned until, after the lapse of several hours, it has acquired the permanent position indicated by the dotted lines P, Q, R in fig. 2, when a piece of cotton-wool should be placed upon the stoppered end and saturated with ether, so as to distil off the liberated carbonic acid, and the application of ether be repeated at intervals until nearly the whole of the carbonate is decomposed and the stoppered end of the tube is full of liquid carbonic acid. If the experiment has succeeded well, a length of the tube, equal to 1 or $1\frac{1}{4}$ inch, will, in cold weather, be filled with the liquid acid. By occasionally (once a day or less) applying the ether to the stoppered end of the tube, that part may

be kept full, or partly full, of liquid acid for a long time; I have kept it in this manner during many months.

6. The most frequent cause of failure is the clogging of the tube with sulphate of ammonia; it is rarely that a leakage occurs at the stopper; and the most frequent causes of explosion are, too rapid generation of the gas, and increased temperature of the atmosphere. It is highly advisable never to examine a charged tube without the wire-gauze intervening to intercept fragments of glass, and to use a large moveable screen of glass to protect the eyes from projected oil of vitriol. Nearly all the explosions which occur take place during the process of generating carbonic acid, or within a few days afterwards. The proportion of tubes fractured or burst at different stages of the process is about one-third.

7. In some experiments, where electric sparks were passed through the liquid acid, two longitudinal cuts $\frac{1}{10}$th of an inch deep, were made by a knife on opposite sides of the gutta-percha plug, extending from its smaller nearly to its larger end, before inserting it in the tube; and two fine platinum wires inserted into the cuts and secured very carefully by means of a heated penknife; the inner end of the plug was then coated with melted paraffin, the plug wetted with paraffin solution, and inserted in the usual manner. The wires extended nearly $\frac{1}{2}$ an inch within the tube, and were imbedded for about $\frac{1}{4}$ of an inch, next to the plug in paraffin, the remaining part served for the electrodes. (See fig. 3.) After inserting the plug and securing it by the binding wires, the whole of the outer end of the plug was freely coated with melted paraffin, to insulate more perfectly the electrodes from each other.

Fig. 3.



8. In a first experiment, the electrodes being $\frac{1}{10}$th of an inch apart, and the liquid acid below 32° Fahr., not the slightest conduction occurred with 40 Smee's batteries; and sparks from a Ruhmkorff's coil which passed through $\frac{3}{8}$ths of an inch of cold air would not pass through the liquid acid. And in a second experiment, with electrodes about $\frac{1}{70}$th of an inch apart, sparks from the coil, which were passing freely through $\frac{9}{32}$nds of an inch of cold air, occasionally passed through the cold liquid acid and exhibited a pale blue colour.

9. These experiments show that liquid carbonic acid is a strong insulator of electricity, and that when prepared with concentrated oil of vitriol, and with the precautions stated, it is free from water, sulphuric acid, and sulphate of ammonia. As further proofs of the freedom of the liquid acid from oil of vitriol and water, it may be mentioned,—1st, that dry extract of litmus exhibited no signs of redness by immersion in the liquid acid; 2ndly, a small fragment of glacial phosphoric acid did not appear at all liquefied, or lose the sharpness of its edges after being immersed several weeks; and 3rdly, anhydrous sulphate of copper did not become at all blue in the liquid acid.

10. The following are the results obtained with various solid substances immersed in the liquid acid; some were immersed during several months, many during several weeks, and a few only during several days. The temperature of the liquid acid was generally a little below that of the external atmosphere. Wood-charcoal remained undissolved and unaltered. Anhydrous boracic acid in powder slightly dissolved. White phosphorus slightly dissolved. Glacial phosphoric acid, green solid biphosphide of hydrogen, and ordinary yellow sulphur, undissolved and unchanged. (Bisulphide of carbon absorbs *gaseous* carbonic acid.) Sulphide of phosphorus, and selenium, undissolved and unaltered. Iodine, biniodide of phosphorus, and iodide of sulphur, all dissolved in small quantities (iodine the most freely), and formed red or reddish solutions. Anhydrous hydrochloric acid (prepared by first half-filling the limb A of the tube with sesquicarbonate of ammonia, and then filling the remaining half with hydrochlorate of ammonia) did not produce two strata in the condensed liquid, but imparted to the liquid a brownish colour in each of two experiments, probably by acting upon the gutta-percha stopper. Pentachloride of phosphorus dissolved slowly and formed a colourless liquid. Metallic potassium and metallic sodium slowly acquired bulky white coatings of alkali. Phosphide of sodium, fused chloride of sodium, phosphide of calcium, anhydrous chloride of calcium, bright metallic aluminium, crystals of silicium, anhydrous silica, silico-fluoride of potassium, and arsenic acid, all remained undissolved and unaltered. Terbromide of arsenic and terbromide of antimony, each dissolved slightly. Hydrated crystals of monosulphate of iron became dehydrated and fell to pieces as a white powder, and did not dissolve. Anhydrous sulphate of copper remained white and undissolved; the hydrated salt became white.

Protochloride of mercury and nitrate of silver remained undissolved and unaltered.

11. Cyanide of mercury, oxalic acid, benzoic accid, succinic acid, pyrogallic acid, gallic acid, tannic acid, tannic acid and potash, paraffin, and cocostearic acid remained undissolved and unaltered in appearance. Pitch softened and partly dissolved. Napthalin dissolved in small quantity. Gutta percha; the liquid acid dissolved out the dark-brown colouring matter, and left the gutta percha undissolved, and much more white. India rubber remained black externally, but became perfectly white through the whole of its thickness; on removing it from the acid, it suddenly swelled to a large size, and gradualiy shrank in a few hours to its orginal dimensions, and afterwards, (in a few days) slowly regained its original colour. Common yellow resin dissolved slightly. Gum-copal remained undissolved. Camphor dissolved rapidly and formed a clear colourless liquid. (Spirit of turpentine dissolves more than its own volume of *gaseous* carbonic acid.) Spermaceti, indigo, pyroxylin, and solid extract of litmus remained undissolved and unaltered. Gamboge dissolved in minute quantity and formed a slightly yellow liquid.

12. These experiments show that liquid carbonic acid is a chemically inert body, and is also a very feeble solvent of substances in general, and is not deoxidized by any of the ordinary deoxidizing agents except the alkali-metals

13. The way to discharge the tubes of their contents is to support them over a gutta-percha vessel within the safety-cage, or behind a duble screen of glass and wire gauze, and, protected by gloves, cut off the binding-wires with a pair of nippers; then if the stoppers are not blown out, pour boiling water upon them. Sometimes the explosion occurs immediately upon cutting the wires, but in most cases it requires the application of the hot water; this is a most convincing proof of the tightness of the stoppers, as the pressure of liquid carbonic acid (according to different authorities) varies from 500 to 1,100 pounds per square inch, according to the temperature of the atmosphere. The tubes nearly always break by the violence of the recoil. In many instances a safer plan was adopted; the wires were not cut, but a current of steam was directed upon the stoppers until they were expelled; the discharge was then less sudden, and the tubes were less frequently broken. It would probably be a still further improvement if the lower end of the tube were closed by a stopper in a

similar manner to the upper end; the contents of the tube might then be discharged at that end, and the substances operated upon would then be exposed to less risk of being lost, and of being brought into contact with the acid and saline matters by the discharge.

XXXI.—*On the influence of Atmospheric Pressure upon some of the Phenomena of Combustion.*

By Dr. E. Frankland, F.R.S.

(Abstracted from the Philisophical Transactions for 1861, by the Author.)

In his classical researches upon flame, Davy mentions the influence which compression and rarefaction exert upon combustion in atmospheric air. Speaking of his experiments with compressed air, the performance of which presented considerable difficulties, he says*, "They show sufficiently that (for certain limits at least) as rarefaction does not diminish considerably the heat of flame in atmospherical air, so neither does condensation considerably increase it; a circumstance of great importance in the constitution of our atmosphere, which at all heights or depths at which man can exist, still preserves the same relations to combustion." His attention was also arrested by the light evolved under similar circumstances, although this phase of the subject does not seem to have attracted more than his cursory attention, and he does not appear to have made any exact quantitative determinations of the rate of increase or diminution of the light of combustion. In reference to this point he says†, "Both the heat and light of the flames of the taper, of sulphur, and of hydrogen were increased by acting on them by air condensed four times; but not more than they would have been by an addition of $\frac{1}{5}$ of oxygen." And again‡, "The intensity of the light of flames in the atmosphere is increased by condensation and diminished by rarefaction, apparently in a higher ratio than their heat, more particles capable of emitting light exist in the denser atmospheres, and yet most of these particles in becoming capable of emitting light, absorb heat; which could not be the case in the condensation of a pure supporting medium."

* Philosophical Transactions for 1817, p. 65.
† Ibid. p. 64. ‡ Ibid. p. 75.

M. Triger, a French Engineer*, records some observations on combustion in compressed air, which were made during some engineering operations of a peculiar kind, carried on in working a bed of coal lying beneath the alluvium on the banks of the river Loire. A stratum of quicksand 59 to 62½ feet thick had to be penetrated; and it was consequently necessary to find some means of excluding the quicksand and water, which it was found impossible to keep out by the ordinary coffer dams. To overcome this difficulty, M. Triger ingeniously employed strong wrought-iron cylinders about 3¼ feet diameter, open below and closed at top. These were gradually sunk in the quicksand, whilst the air inside them was compressed to the necessary extent to exclude the outer semifluid matter. The workmen labouring within these cylinders were exposed to a pressure of about three atmospheres; and it was observed that the candles, by which they were lighted, burnt with much greater rapidity than at ordinary atmospheric pressure. Respecting this rapid combustion M. Triger says, "A la pression de trois atmosphères, cette accélération devient telle que nous avons été obligés de renoncer aux chandelles à mêches de coton pour les remplacer par des chandelles à mêches de fil. Les premiéres brulaient avec une telle rapidité qu'elles duraient à peine un quart d'heure, et elles répandaient en outre une fumée intolerable."

An observant officer of artillery stationed in India, Quartermaster Mitchell, found that the time of burning of the fuses of shells was considerably increased from the diminution of atmospheric pressure at elevated stations. To the results of his experiments I shall presently have to refer in detail.

Finally, J. Le Conte†, in his interesting memoir on the influence of solar light on combustion, expresses the following opinion with reference to the observations of Davy, Triger, and Mitchell: "Thus a variety of well established facts concur in fortifying the conclusions to which we are led by *à priori* reasoning namely, that the process of combustion is retarded by diminution of the density of the air, whilst it is accelerated by its condensation." M. Le Conte did not himself make any experiments on the influence of atmospheric pressure on the rate of combustion.

Such was the state of knowledge and opinion regarding the influence of atmospheric pressure upon the heat and light of

* Ann. Ch. Phys. [3] iii. 234, 1841.

† Silliman's American Journal of Science and Arts [2] xxiv. 317.

combustion, when in the autumn of 1859, whilst accompanying Dr. Tyndal to the summit of Mont Blanc, I undertook some experiments on the effect of atmospheric pressure upon the rate of combustion of candles.

I. INFLUENCE OF ATMOSPHERIC PRESSURE ON THE RATE OF COMBUSTION.

a. Of Candles.

In the experiments just alluded to, six stearin candles were first burnt for one hour at Chamonix, the amount of stearin consumed being carefully determined for each candle: the same candles were afterwards burnt for one hour, carefully protected from currents of air, in a tent on the summit of Mont Blanc, the consumption of stearin being again ascertained. The following were the mean numbers obtained :—

At Chamonix . .	9·4 grms. stearin per hour.
Summit of Mont Blanc.	9·2 grms. stearin per hour.

This close approximation of the two results under such widely different atmospheric pressures, goes far to prove that *the rate of combustion of candles is entirely independent of the density of the air*, the slight discrepancy being probably attributable to the difference (21° C.) of atmospheric temperature in the two series of experiments. It is impossible to repeat these determinations in a satisfactory manner with artificially rarefied atmospheres, owing to the heating of the apparatus which surrounds the candle, and the consequent guttering and unequal combustion of the latter. But in an experiment with a sperm candle, which was burnt first in air under a pressure of 28·7 inches of mercury, and then in air at 9 inches pressure, other conditions being as similar as practicable in the two experiments, the consumption of sperm was found to be,—

At pressure of 28·7 inches .	7·85 grms. of sperm per hour.
At pressure of 9·0 inches .	9·10 grms. of sperm per hour.

This experiment, unsatisfactory as it was in several respects, tends to confirm, for higher degrees of rarefaction, the result previously obtained.

β. Of Time-fuses.

In a letter dated January 6th, 1855, an extract from which appeared in the "Proceedings of the Royal Society*," Quarter-

* Vol. vii. p. 316.

master Mitchell communicated the results of a series of carefully conducted experiments, proving that the rate of combustion of the fuses of shells was subject to considerable retardation, which he attributed to the diminution of atmospheric pressure at elevated stations, causing a more scanty supply of oxygen. The following is a short statement of the results of these experiments, in which three-inch fuses were burnt under different atmospheric pressures :—

	Height of barometer at 0° C.	Elevation above sea-level.	Time of burning.
	inches.	feet.	seconds.
1. Average of 6 experiments..	29·61	....	14·25
2 Average of 6 experiments .	26·75	3000	15·78
3 Average of 4 experiments..	23·95	6500	17·10
4 Average of 2 experiments..	22·98	7300	18·125

Comparing the amount of retardation with the corresponding reduction of pressure, we have the the following results :—

Numbers of experiments between which comparison is made.	Diminution of pressure.	Retardation of combustion.
	inches.	seconds.
1 and 2	2·86	1·53
2 and 3	2·80	1·32
3 and 4	·97	1·025

Although the results, as I shall presently endeavour to show are perfectly compatible with those obtained with candles under similar circumstances, yet the subject seemed to me of sufficient technical importance to warrant a repetition and extension of these experiments in artificially rarefied air. For this purpose a large iron cylinder was connected on the one hand with an air pump, and on the other with a piece of gas-pipe 6 feet long and 4 inches internal diameter, the opposite end of the pipe being furnished with an arrangement by which the end of the fuse to be ignited could be introduced air-tight within the pipe, whilst the closed end of the fuse projected about 2 inches into the external air. The fuses were ignited at a given instant by a voltaic arrangement,

consisting of ten cells of Grove's battery, an instantaneous contact maker, and a piece of thin platinum wire which was inserted into the priming of the fuse. In order to ascertain with precision the moment when the deflagration was finished, the lateral hole at the posterior end of the fuse was bored through to the opposite side: a piece of thread was passed vertically through this aperture, and secured above to a convenient support, whilst an iron ball was affixed to its lower extremity at a distance of a few inches above an iron plate, upon which the ball fell when the fire reached the thread, thus indicating the moment when under ordinary circumstances, the fire of the fuse would be communicated to the contents of the shell. The pressure was indicated by a mercurial gauge inserted into the gas pipe.

The experiments were made with 6-inch fuses (for which I was indebted to the kindness of my friend Mr. Abel of the Woolwich Royal Arsenal), in the following manner. The fuse being inserted into the end of the gas-pipe, and the necessary degree of exhaustion in the iron cylinder and pipe having been obtained, the fuse was ignited at a given signal. During the continuance of its deflagration, an assistant worked the air-pump so as to prevent any great rise in pressure, whilst another observed the vacuum gauge at the moment when the iron ball dropped. The mean between the pressure at the commencement of the deflagration, and that at the end, was assumed to be the mean pressure under which the fuse had been burnt: but it is obvious that this assumed mean pressure can only be approximative, although the gauge fell very regularly and gradually during the continuance of the deflagration.

The following average results were obtained:—

Average pressure, in inches of mercury.	Average time of deflagration of 6-inch fuse.	Increase of time of burning over preceding observation.	Reduction of pressure corresponding with increase of time.	Increase of time for each diminution of 1-inch pressure.
	seconds.	seconds.	inches.	seconds.
30·40	30·33			
28·25	32·25	1·92	2·15	·893
25·70	34·75	2·50	2·55	·980
22·45	37·75	3·00	3·25	9·25
19·65	41·50	3·75	2·80	1·339
15·95	45·50	4·00	3·70	1·081

There are here evident indications of the rate of retardation being somewhat greater at low than at comparatively high pressures; but, neglecting these indications, the above numbers give 1·043 second as the average retardation in a six-inch or thirty-seconds fuse for each inch of mercurial pressure removed. This result agrees closely with that obtained by Quartermaster Mitchell, if we except those fuses which he burnt at the greatest altitude, and in reference to which some error must obviously have crept in, either as regards the altitude of the station where the fuses were burnt, or the duration of their combustion. The latter source of error is perhaps rendered less improbable, from the fact that only two experiments were made at the greatest altitude, whilst six were performed at two, and four at the third of the remaining stations. The following table shows Mr. Mitchell's results, uniformly with those in the last table. The fuses which he employed being fifteen-seconds or three-inch ones, I have multiplied their times of combustion by two, in order to bring them into comparison with the six-inch fuses which were used in my experiments :—

Pressure in inches of mercury.	Average time of combustion of 6-inch fuse.	Increase of time of combustion over last observation.	Reduction of pressure corresponding to increase of time.	Increase of time for each diminution of 1-inch pressure.
	seconds.	seconds.	inches.	seconds.
29·61	28·50			
26·75	31·56	3·06	2·86	1·070
23·95	34·20	2·64	2·80	·943
22·98	36·25	2·05	·97	2·113

Here, omitting the last determination as abnormal, we have the average retardation, in the combustion of a six-inch fuze, equal to 1·007 second for each diminution of one-inch mercurial pressure, which coincides almost exactly with the number (1·043) deduced from my own experiments.

The results of both series of observations may therefore be embodied in the following law :—*The increments in time are proportional to the decrements in pressure.*

For all practical purposes the following rule may be adopted :—*Each diminution of one inch of barometrical pressure causes a*

retardation of one second in a six-inch or thirty-second fuse. Or, *each diminution of atmospheric pressure to the extent of one mercurial inch increases the time of burning by one-thirtieth.*

This retardation in the burning of time-fuses by the reduction of atmospheric pressure, will probably merit the attention of artillery officers. These fuzes have hitherto been carefully prepared so as to burn at Woolwich, a certain number of seconds, and the perfection with which this is attained is highly remarkable; but such time of combustion at the sea-level is no longer maintained when the fuses are used in more elevated localities. The ordinary fluctuations of the barometer in our latitude must render the rate of combustion of these fuses liable to a variation of about ten per cent. Thus a fuse driven to burn 30 seconds when the barometer stands at 31 inches, would burn 33 seconds if the barometer fell to 28 inches. The height to which a shell attains in its flight must exert an appreciable influence upon the burning of its time fuse; to a far greater extent, however, must the time of combustion be affected by the position of the fuse during the flight of a rifled shell: as in these projectiles the fuse always precedes the shell, the time of burning must obviously be very much shorter than when the shell and fuse are at rest. In an ordinary shell which rotates upon a horizontal axis, the alternate compression and rarefaction of the air at the mouth of the fuse, although tending to compensate each other, will still leave a considerable balance of compression, which must cause a marked retardation in the rate of burning.

The apparently opposite conclusions to which we are led as regards the influence of atmospheric pressure upon the *rate* of combustion, by the experiments upon candles on the one hand and upon time-fuses on the other, are by no means irreconcileable; in fact, an examination into the conditions of combustion in the two cases scarcely leaves room for the expectation of any other result.

In the combustion of a candle, the radiant heat from the flame first melts the combustible matter in the capsule at the base of the exposed portion of the wick; the capillary action of the latter then elevates the liquefied wax, tallow, or spermaceti into the upper part of the wick, where it is exposed to a temperature which effects its volatilization and decomposition. It is thus

evident that the rate of combustion, or at all events the rate of consumption of the combustible matter of the candle, is entirely dependent upon the capillarity of the wick, provided that the radiant heat from the flame is sufficient to keep up a supply of liquefied combustible matter at the base of the wick, and that the temperature of the flame is high enough to volatilize this matter on its arrival near the apex of the cotton. Now as capillary attraction is not altered by variations of atmospheric pressure, and as the temperature of the flame is, as will be shown below, almost entirely independent of the same influence, a diminution in the consumption of combustible matter could only arise from the amount of radiant heat striking the capsule at the base of the wick being insufficient to keep up a supply of melted combustible matter equal to the capillary demands of the wick. There can scarcely be a doubt that the amount of heat radiated from a given area of the lower surface of the flame is diminished by rarefaction owing to the decreasing luminosity of the flame: nevertheless this diminution is compensated by the increased flame surface, the radiant heat from which strikes the capsule when the flame becomes enlarged by rarefaction. Whether this compensation be complete or not is of little importance, since observation shows that, even at the highest degrees of rarefaction, a sufficient amount of heat reaches the capsule to keep up an abundant supply of liquefied combustible matter.

We have therefore no ground for any *à priori* assumption that the combustion of candles ought to go on at a decreased rate in rarefied air; in fact there is one consideration which might lead to the opposite opinion; it is this,—the rapidity of the consumption of a candle obviously depends upon the amount of liquefied wax, &c., which passes up its wick in a given time: this amount is determined, up to a certain maximum limit, by the rapidity with which it is got rid of at the upper portion of the capillary tubes where it is volatilized by the heat of the flame. Now, as the rapidity of volatilization is known to be increased by a reduction of pressure, it follows that a larger amount of the combustible would be thus removed from the upper portion of the wick in rarefied than in compressed air. Nevertheless this influence of reduced pressure must be very small in the case of bodies possessing such high boiling-points as tallow, wax, &c., and hence its influence upon the rate of combustion in rarefied air cannot be perceived.

Opposed to the above facts and considerations stands the observation of M. Triger, that candles burn much more rapidly in air compressed three times, than in air at the ordinary pressure. This discrepancy, the cause of which can now only be conjectured, may perhaps reside in some of the circumstances, described above, under which the experiments were made. The constant supply of compressed air to a chamber such as that in which the candles were burnt, must have occasioned a comparatively high temperature in the atmosphere of the chamber, necessarily causing the candles to gutter. Further, the very imperfect combustion which a candle undergoes at this high pressure would have a tendency to increase the size of that portion of the wick situated within the flame, and which constitutes the surface from which the evaporation of the combustible proceeds. Both these circumstances would, I conceive, practically tend greatly to shorten the time during which a candle would burn, which was precisely the circumstance that alone attracted M. Triger's attention, no quantitative determinations of the weight of combustible matter *actually consumed* having been made.

In the deflagration of time-fuses, the conditions are obviously very different. Here the combustible matter never comes into contact with atmospheric oxygen until it has left the fuse-case; unlike the candle, the composition contains within itself the oxygen necessary for combustion, and a certain degree of heat only is necessary to bring about chemical combination. If this heat were applied simultaneously to every part of the fuse composition, the whole would burn almost instantaneously. This sometimes approximately occurs, when, by the expansion of the wooden case into which the composition is rammed, a slight space is formed between the case and its contents, thus allowing the deflagration to propagate itself between the case and the composition. Under such circumstances the fuse burns with explosive rapidity; and probably the occasional bursting of shells before, or immediately after leaving the guns, may be due in some cases to this cause. Under normal circumstances, however, the fuse burns only at a disc perpendicular to its axis; and the time occupied in its deflagration necessarily depends upon the rapidity with which each successive layer of composition is heated to the temperature at which chemical combination takes place. This heat, necessary to deflagration, is evidently derived from the products of the combustion of the immediately preceding layer of

composition; and the amount of heat thus communicated to the next unburnt layer must depend, in great measure, upon the number of particles of these heated products which come into contact with that layer. Now, as a large proportion of these products are gaseous, it follows that, if the pressure of the surrounding medium be reduced, the number of ignited gaseous particles in contact at any one moment with the still unignited disc of composition will also be diminished. Hence the slower rate of deflagration in rarefied air.

II. INFLUENCE OF ATMOSPHERIC PRESSURE ON THE LIGHT OF COMBUSTION.

a. Influence of Rarefaction.

In burning candles upon the summit of Mont Blanc, I was much struck by the comparatively small amount of light which they emitted. The lower and blue portion of the flame, which, under ordinary circumstances, scarcely rises to within a quarter of an inch of the apex of the wick, now extended to the height of one-eighth of an inch above the cotton, thus greatly reducing the size of the luminous portion of the flame.

On returning to England, I repeated the experiment under circumstances which enabled me to ascertain, by photometrical measurements, the extent of this loss of luminosity in rarefied air. The result proved that a great reduction in illuminating effect ensues when a candle is transferred from air at the ordinary atmospheric pressure to rarefied air. At the same time, remarkable, changes in appearance occur in the flame itself, especially at high degrees of rarefaction. During the diminution of pressure down to half an atmosphere, the chief alteration is the gradual invasion of the upper and luminous portion of the flame, by the lower blue and non-luminous part. As the pressure sinks towards 10 inches of mercury, the retreat of the luminous portion of the the flame towards the apex goes on uninterruptedly, but the shape and colour of the flame also begin to undergo very remarkable alterations; the summit becomes more and more rounded, until at 10 inches pressure the flame assumes nearly the form of an ellipse, whilst the blue portion, which now comprises nearly the whole flame, acquires a peculiar greenish tint. Finally, at 6 inches

pressure, the last trace of yellow disappears from the summit of the flame, leaving the latter an almost perfect globe of the peculiar greenish-blue tint above-mentioned. Just before the disappearance of the yellow portion of the flame, there comes into view a splendid halo of pinkish light, forming a shell half-an-inch thick around the blue-green nucleus, and thus greatly enlarging the dimensions of the flame. The colour of this luminous shell closely resembles that first noticed by Gassiot in the stratified electrical discharge passing through a nearly vacuous tube containing a minute trace of nitrogen. The colour thus imparted to the electrical discharge undoubtedly constitutes the most delicate test of the presence of nitrogen. In both cases, I believe the coloured light to be due to incadescent nitrogen. Under a pressure of 4·6 inches of mercury, a small gas-flame burning in a glass chimney, $1\frac{1}{4}$ inch in diameter nearly fills the latter with the pinkish glow just mentioned, which extends to a height of nearly 3 inches above the true flame, forcibly reminding the observer of the electrical discharge through a nearly vacuous tube. The gas-flame did not manifest any tendency to extinction at this low pressure.

In attempting photometrical determinations with candles, it was found that, owing to the irregularities of combustion already noticed, no satisfactory quantitative experiments could be made in artificially rarefied air. Oil lamps proved also equally unsuitable, owing to the gradual ascent of the base of the flame towards the apex of the wick, by which the size of the flame and the hourly consumption of oil were greatly diminished. Recourse was therefore had to coal gas, which, although liable to certain minor disturbing influences, yet yielded results, during an extensive series of experiments, exhibiting sufficient uniformity to render them worthy of confidence.

The apparatus employed consisted of a governor into which the gas was first led, and whence it issued through a T-piece, one branch of which led to a jet which I will call *the standard flame*, at one extremity of a Bunsen's Photometer, whilst the other communicated with a test-meter supplying a second jet which may be conveniently termed *the experimental flame*, and which was placed at the opposite extremity of the photometer; thus the delivery of gas of uniform pressure, at the two stopcocks regulating the supply to the two flames, was secured. The standard flame was shielded from currents of air by a cylindrical glass shade. The vessel or receiver, in which the experimental flame was made to burn under

different atmospheric pressures, consisted of a glass cylinder 12 inches high and 4½ inches in diameter, welted and ground at both ends, which could be closed air-tight by ground cast-iron plates, between which and the ends of the cylinders collars of leather were introduced, so as to distribute more evenly the pressure exerted by the nuts and screws of the three steel rods binding together the upper and lower plates. The experimental flame burnt within a glass chimney contracted at top and cemented with plaster of Paris into a stopcock, which opened a communication for the exit of the products of combustion; a similar stopcock inserted into the under plate, served for the admission of air into the cylinder. The gas-delivery tube for the experimental flame passed air-tight through a stuffing box in the upper cover of the cylinder, and was most carefully united with the exit tube of the meter so as to exclude the admission of any trace of air during the experiments, and especially whilst the gas was being consumed under reduced pressure.

The atmosphere within the glass cylinder could be uniformly maintained at any pressure from that of the atmosphere downwards, by means of an air-pump and a cylindrical reservoir. The latter was constructed of wrought iron, and, having a capacity of 2¾ cubic feet, served to maintain a very constant pressure unaffected by the intermittent action of the air-pump. The pressure in the reservoir, and consequently in the glass cylinder was indicated by a gauge, which was usually worked with mercury, but occasionally, as described below, with water.

Such is a general outline of the arrangement of the apparatus used: but the following additional particulars may serve to illustrate more fully the mode in which the experiments were conducted. The test-meter was constructed in the usual manner so as to show, by observations of one minute's duration, the rate of consumption per hour; but, in order to ensure greater accuracy, these observations were always extended over a space of at least five minutes, and were repeated at intervals during the course of the determinations at each particular pressure. In order to have the rate of admission of gas to the experimental flame perfectly under control, a micrometer stopcock was inserted in the exit-tube of the meter. Just above the internal orifice of the stopcock for the admission, was placed a circular disc, so as to prevent the current of air from impinging upon the experimental flame; by this arrangement, the latter always burnt with perfect steadiness.

It is well known that the illuminatiug effect of a gas-flame depends very considerably upon the velocity of the current of air in which it burns, and that the maximum illuminating effect is always produced when the velocity of the current of air is only just sufficient to prevent the escape of unconsumed fuliginous matter; in other words, a maximum of light is obtained from a gas-flame, other things, being equal, when that flame is maintained just below the *smoking point*. This condition of maximum luminosity was carefully secured in all the following determinations, by regulating the admission of external air, and thereby the velocity of the current in the chimney, which was always in free communication with the reservoir and air-pump. When, however, the experimental flame was burning at atmospheric pressure, the cock for the admission of air was removed, leaving a large aperture, whilst the current through the chimney was regulated by the cock at the top of the latter. The extremity of the gas-delivery tube was narrowed to a circular aperature 1·5 millimetre in diameter (about $\frac{1}{17}$th inch), thus forming a burner of such magnitude, as not only to prevent the gas from being discharged from the jet with more than the smallest possible pressure, but also to render the difference of pressure between the gas in the delivery-tube and the air in the glass cylinder practically the same in all the observations.

Each series of experiments was made in the following manner:—The standard flame was lighted, and its rate of consumption regulated to about ·6 or ·7 cubic foot per hour. The absolute amount of gas consumed by this flame was obviously not material, provided that its rate of consumption and conditions of combustion did not vary during the continuance of any one series of experiments. This constancy in the rate and conditions of combustion was secured by the governor. The exhaust cock being closed, and the pressure in the glass cylinder reduced to about 6 inches of mercury, the air-inlet cock was removed, the exhaust cock slightly opened, and the experimental flame ignited by the introduction of a small taper through the open aperature from which the air-inlet cock had been removed: the latter cock was then replaced, and gradually turned so as to cut off all but the necessary supply of air, whilst the exhaust cock was at the same time gradually opened so as to equalize the pressure in the glass cylinder and in the reservoir. With this diminution of pressure in the glass cylinder, it was of course necessary simultaneously to reduce the size of the aperture through which the gas passed from the meter to the burner; and

this was effected by a micrometer cock attached to the test-meter. The pressure was now allowed to rise until it reached the lowest point at which a series of observations was to be made: at this point it was then maintained constant by the steady working of the air-pump. The consumption of gas in the experimental flame having been now accurately adjusted to ·65 cubic foot per hour, and all extraneous light excluded from the room, a preliminary observation was made of the illuminating power of the experimental flame as compared with the standard. Owing to the gradual heating of the apparatus surrounding the experimental flame, the temperature, and consequently the luminosity of the latter, underwent a gradual and not unimportant increase, which continued for about an hour, when the illuminating power became perfectly constant. As soon as this constancy of light had been obtained, twenty observations of the illuminating power were made. The pressure in the glass cylinder was then suffered to rise to the point at which the next observations were to be made. The consumption of gas was again carefully adjusted to ·65 cubic foot per hour, when twenty photometrical observations were again made. Similar sets of observations at the remaining higher pressures up to the full atmospheric pressure completed the series.

In the following mean tabulated results, the illuminating power of the standard flame is assumed to be 100, whilst the numbers given under the several pressures represent the luminosity of the experimental flame compared with this standard. In all the series of observations, the consumption of gas by the experimental flame was ·65 cubic foot per hour, measured at the atmospheric pressure :—

First Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver =

6·6 in. mercury.	9·6 in. mercury.	14·6 in. mercury.	19·9 in. mercury.	24·9 in. mercury.	29·9 in. mercury.
1·1	6·5	24·2	63·5	90·0	119·97

Second Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver =

10·2 in. mercury	12·2 in. mercury	14·2 in. mercury	16·2 in. mercury	18·2 in. mercury	20·2 in. mercury	22·2 in. mercury	24·2 in. mercury	26·2 in. mercury	28·2 in. mercury	30·2 in. mercury
4·3	14·9	23·6	34·9	44·4	56·8	72·9	86·8	95·7	108·6	118·8

In order to bring the two series of observations into more strict comparison with each other, and with following determinations, it will be convenient to reduce the mean experimental numbers to a standard of illuminating power, in which the light at the maximum pressure, that is the full atmospheric pressure, is assumed to be 100. We then get the following numbers:—

First Series.

Pressure of air in receiver in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.
29·9	119·97	100·0
24·9	90·0	75·0
19·9	63·5	52·9
14·6	24·2	20·2
9·6	6·5	5·4
6·6	1·1	·9

Second Series.

Pressure of air in receiver in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.
30·2	118·8	100·0
28·2	108·6	91·4
26·2	95·7	80·6
24·2	86·8	73·0
22·2	72·9	61·4
20·2	56·8	47·8
18·2	44·4	37·4
16·2	34·9	29·4
14·2	23·6	19·8
12·2	14·9	12·5
10·2	4·3	3·6

These numbers show that even the natural oscillations of atmospheric pressure produce a considerable variation in the amount of light emitted by gas-flames; and, as such a variation is of interest from a technical point of view, it appeared to me of sufficient importance to warrant a special series of observations within, or nearly within, the usual fluctuations of the barometrical column. In order to attain greater delicacy in the pressure-readings in these experiments, a water-gauge was substituted for a mercurial one, but its indications are translated into inches of mercury in the following tabulated results :—

Third Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver =

27·2 in. of mercury.	28·2 in. of mercury.	29·2 in. of mercury.	30·2 in. of mercury.
70·3	74·7	79·2	83·4

Reducing the means of these results, as before, to the maximum standard of 100, we have the following numbers :—

Third Series.

Pressure of air in receiver in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.
30·2	83·4	100·0
29·2	79·2	95·0
28·2	74·7	89·6
27·2	70·3	84·3

It is thus evident that the combustion of an amount of gas which will give a light equal to 100 candles when the barometer stands at 31 inches, will yield light equal only to 84·3 candles when the barometer falls to 28 inches. Such a variation in the luminosity of gas-flames with the oscillations of the barometer

will obviously elude the ordinary modes of taking the illuminating power of gas, inasmuch as the standard light with which the gas is compared is also subject to the same influence. Still, although the relative light of gas as compared with candles may remain nearly or quite unaltered, yet its absolute illuminating value depends greatly upon the height of the barometer at the place where it is burnt. Thus a quantity of coal-gas which in London would yield a light equal to 100 candles, would, if burnt in Munich, give an illuminating effect equal to little more than 91 candles; whilst if used to light the city of Mexico, its luminosity would be reduced to 61·5 candles. These numbers are independent of the change of volume by reduced pressure. If equal volumes of the same sample of coal-gas were consumed in London and Mexico, the illuminating effects would be as 100 : 46·2, the temperature being the same in both cases.

An inspection of the above three series of observations, reveals the fact that the rarefaction of air, from atmospheric pressure downwards, produces a uniform diminution of light until the pressure is reduced to about 14 inches of mercury, below which the diminution of illuminating power proceeds at a less rapid rate. This uniformity of relation between pressure and luminosity will be more clearly seen from Diagrams 1 and 2, in which the luminosity is represented by the ordinates, and the pressure by the abscissæ measured from the origin B. If therefore the luminosity were simply proportional to the pressure, the curve of luminosity would coincide with the diagonal drawn from A to B in diagram No. 1. Inasmuch, however, as the diminution of light is more rapid than the diminution of pressure, the lines A C and A D, representing the experimental results of the first and second series of observations, fall between this diagonal and the ordinate corresponding to the point A. Diagram No. 2 shows the results of the third series of observations; in order to render it as open as possible, only that portion of the square is given through which the experimental line A B passes. The line A C in Diagram No. 1, represents the average results of the first series of observations, whilst A D indicates those of the second series. It will be seen, from an inspection of both series, not only that the lines are nearly coincident, but that they do not, down to 14 inches pressure, deviate much from a straight path. This is obviously due to an equal, or nearly equal diminution of light for each equal decrement of pressure down to about 14 inches, below which pressure

Diagram N°. I.

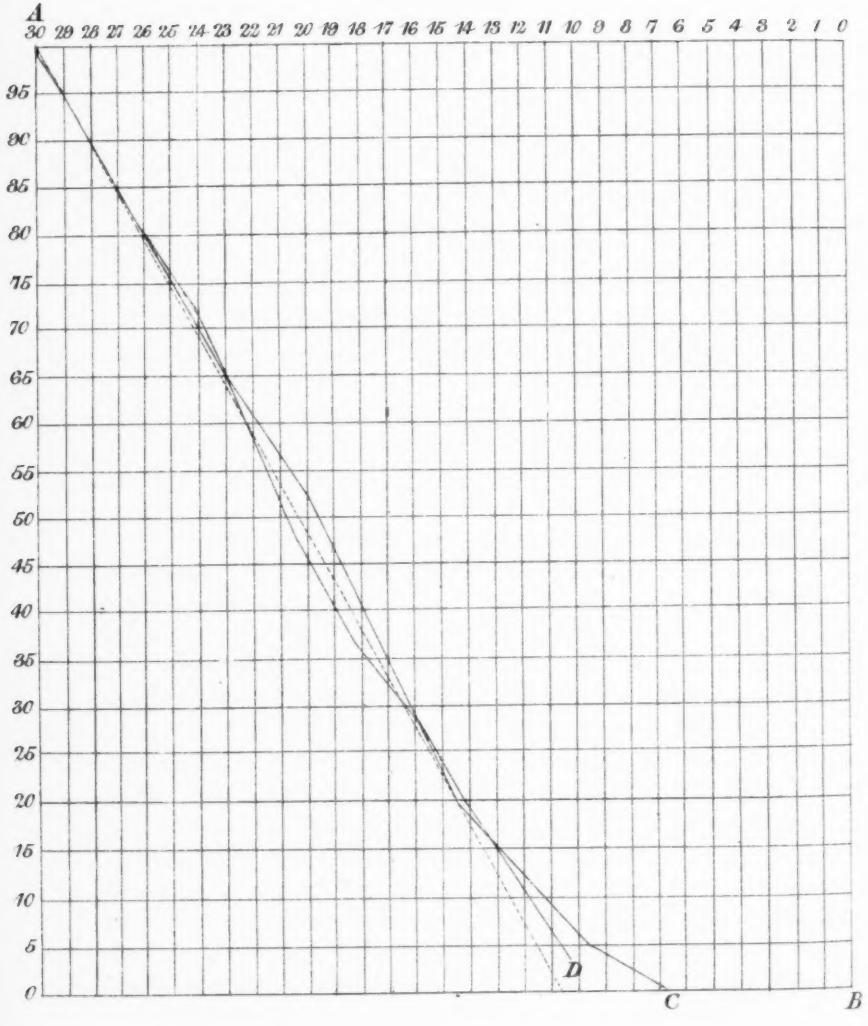
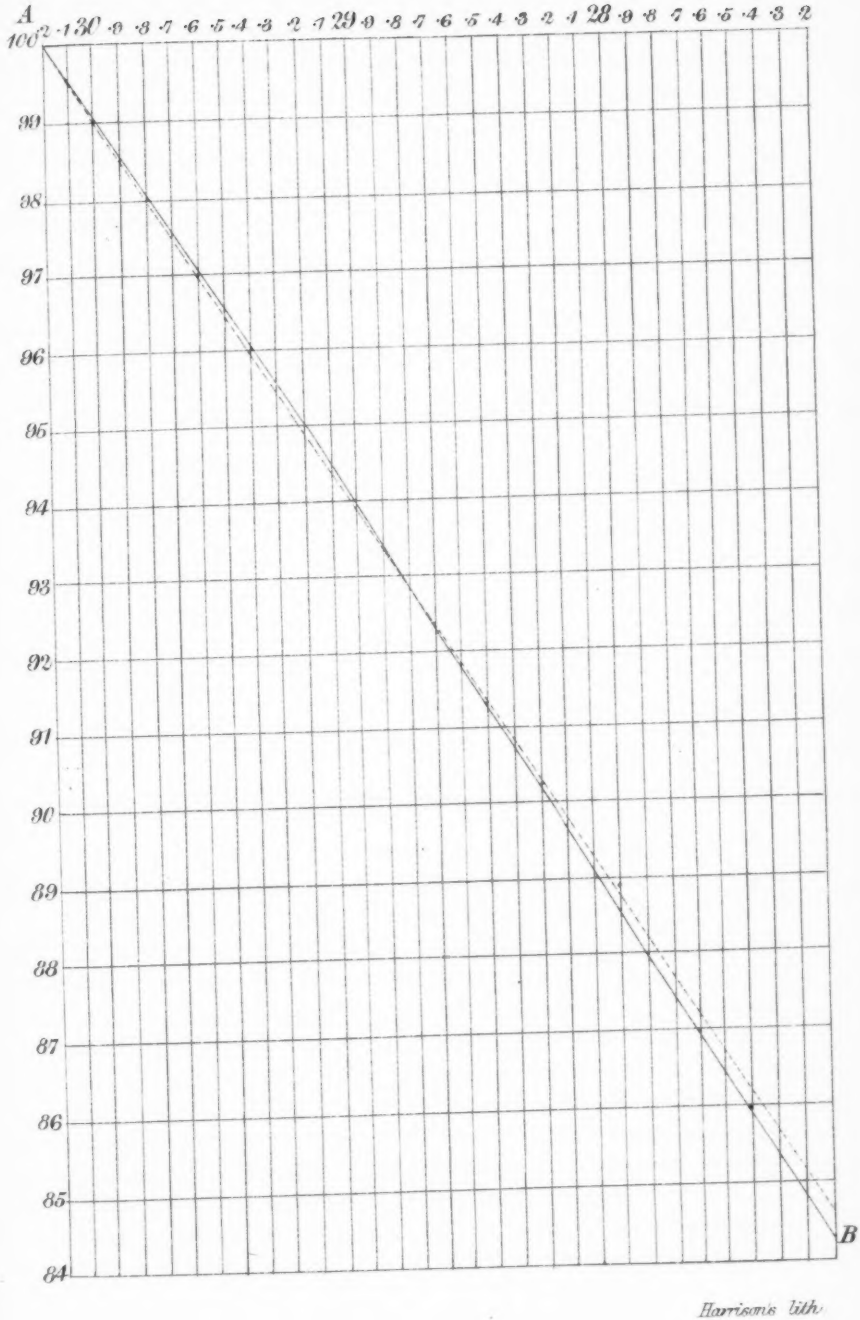

A
30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
D
C
B

Diagram N° II.


A
100
99
98
97
96
95
94
93
92
91
90
89
88
87
86
85
84
B
Harrison's lith

both lines deviate markedly from their previous direction, indicating an alteration in the rate of the diminution of luminosity. The mean results of the three series of observations give approximately 5·1 per cent. of the luminosity at 30 inches pressure as the diminution of light corresponding to each diminution of 1 inch of mercurial pressure down to 14 inches. The following Tables exhibit the illuminating effect actually observed, compared with that calculated from this constant:—

First Series.			*Second Series.*			*Third Series.*		
Pressure in inches of mercury.	Illuminating power.		Pressure in inches of mercury.	Illuminating power.		Pressure in inches of mercury.	Illuminating power.	
	Observed	Calculated.		Observed.	Calculated.		Observed.	Calculated.
29·9	100·	100·	30·2	100·	100·	30·2	100·	100·
24·9	75·0	74·5	28·2	91·4	89·8	29·2	95·0	94·9
19·9	52·9	49·0	26·2	80·6	79·6	28·2	89·7	89·8
14·6	20·2	22·0	24·2	73·0	69·4	27·2	84·4	84·7
9·6	5·4	− 3·5	22·2	61·4	59·2			
6·6	·9	−18·8	20·2	47·8	49·0			
			18·2	37·4	38·8			
			16·2	29·4	28·6			
			14·2	19·8	18·4			
			12·2	12·5	8·2			
			10·2	3·6	−2·0			

The dotted lines in Diagrams Nos. 1 and 2 represent the calculated luminosity according to the above Tables. The experimental lines above 14 inches pressure do not, in any part of their course, deviate more from the calculated line than might be expected from the usual errors of experiment. The law of the diminution of the light of gas-flames by reduction of pressure from 30 inches to 14 inches of mercury, may therefore be thus stated. *Of* 100 *units of light emitted by a gas-flame burning in air at a pressure of* 30 *inches of mercury,* 5·1 *units are extinguished by each diminution of one mercurial inch of atmospheric pressure*; or, more generally, *the diminution in illuminating power is directly proportional to the diminution in atmospheric pressure.*

It must, however, here be remarked that the above determinations only establish the constant 5·1 for the particular quality of

gas with which the experiments were performed. It still remained to be ascertained whether a flame from gas of a different quality would be amenable to the same rate of reduction; a fourth series of observations was, therefore, made with gas naphthalized to such an extent as nearly to double its illuminating power. The consumption of gas by the experimental flame was, as before, ·65 cubic foot per hour. The following results were obtained:—

Fourth Series.

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure of air in receiver=

6·9 in. of mercury.	9·9 in. of mercury.	14·9 in of mercury.	19·9 in of mercury.	24·9 in. of mercury.	29·9 in. of mercury.
1·00	7·42	28·24	55·54	85·58	114·95

The following Table, calculated from the above, shows that these results are completely in harmony with those obtained with unnaphthalized gas, thus proving that the rate of diminution of luminosity in rarefied air is the same for all hydrocarbon gases, of whatsoever quality, the last two columns being nearly identical down to 14·9 inches pressure:—

Pressure of air in inches of mercury.	Mean illuminating power. Experimental.	Mean illuminating power. Reduced.	Illuminating power. Calculated.
29·9	114·95	100·	100·
24·9	85·58	74·4	74·5
19·9	55·54	48·3	49·0
14·9	28·24	24·5	23·5
9·9	7·42	6·4	— 2·0
6·9	1·02	·9	—17·3

This series was continued down to 4·6 inches pressure, but the illuminating power of the flame could then no longer be measured by the photometer.

β. Influence of Compression.

The foregoing experiments having demonstrated a very remarkable diminution of light in candle and gas-flames by a reduction of atmospheric pressure, it became interesting to ascertain the effect of compressed air upon the luminosity of similar flames. At the very outset of this part of the inquiry, considerable difficulties presented themselves, since it became necessary to abandon a gaseous combustible which could not be compressed to the necessary degree, and then delivered at a uniform pressure through a burner without very complex apparatus. I was thus compelled to resort to solid or liquid combustibles, the irregularities of which were still further increased by the space within the combustion-chamber being necessarily more confined, in order that its walls might the better sustain high pressures. These difficulties in the way of accurate determinations were, however, by no means the most formidable; for it was soon found that any considerable increase of atmospheric pressure caused both candle and oil-flames to throw off large quantities of fuliginous matter, the formation of which could not be prevented by any amount of draught that could be established in the chimney of the apparatus. Hence, although the luminosity of the flames was greatly increased, yet it was obviously much less so than would have been the case under conditions of more perfect combustion. In fact it soon became evident, that the determinations of increase of luminosity by compression must be made in a manner precisely the reverse of that employed for the corresponding determinations in rarefied air; for, whilst in the latter case, the experiments were made with flames, which at ordinary atmospheric pressure were saturated with carbon particles, in the former it was found necessary to commence with flames which were very feebly, or not at all luminous at common pressures. Such is the effect of compressed air in determining the precipitation of carbon particles within the flame, that a small alcohol lamp, which at the ordinary pressure burnt with a pure blue flame, became highly luminous when placed under a pressure of four atmospheres; and it can scarcely be doubted that, at a

pressure of five or six atmospheres, its luminosity would be equal to that of sperm oil burning at atmospheric pressure.

The apparatus employed was very similar to that used in the previous part of the inquiry, the gas-delivery tube being replaced by a small lamp, and the comparatively thin and wide cylinder used in the rarefaction experiments by a stronger one, 12 inches long, 2 inches internal diameter, and $\frac{5}{8}$ inch thick. The air was compressed by a forcing pump into a strong reservoir from which it was admitted into the experimental receiver by the air-inlet cock before described, whilst the products of combustion escapes through the exhaust cock which was now made to open into the atmosphere.

The experiments were made in the following manner. The upper cover of the receiver being removed, and the reservoir charged with compressed air, a gentle stream of the latter was turned into the receiver. The lamp was now lighted, and the cover firmly screwed into its place, the exhaust or exit cock being wide open. The admission of air was then regulated so as to produce in the chimney that degree of draught necessary for obtaining the maximum amount of light in the experimental flame. After the latter had been allowed to burn for about half an hour, so as to bring the surrounding glass to a temperature which afterwards remained tolerably uniform, a series of photometrical observations were made. The egress of air through the exit cock was then gradually diminished, whilst the air-inlet cock was fully opened, so as to establish a free communication, and consequently an equality of pressure, between the reservoir and the receiver. The pressure, as indicated by a mercurial gauge was now adjusted, by the more or less rapid working of the pump, to that required for the next series of observations. In practice it was found impossible, with the same liquid in the lamp, to extend any series of observations over a greater range than one atmosphere, owing to the experimental flame beginning to smoke at the higher pressure, if it possessed a measurable illuminating power at the lower one.

Owing to the difficulties above mentioned, I have only been able to obtain satisfactory determinations between one and two atmospheres. In these determinations, the lamp was supplied with amylic alcohol—a liquid which, whilst affording an appreciable amount of light in the experimental flame under one-atmosphere pressure, was found to burn under two atmospheres without smoke, although at a somewhat higher pressure it began to evolve

unconsumed carbon. The following mean results were obtained:—

Illuminating power of Experimental Flame compared with Standard Flame at 100.

Pressure in receiver in inches of mercury =

29·7 inches.	59·7 inches.	59·5 inches.
21·2	55·9	55·4

These numbers approximate to those calculated in accordance with the law already given for pressures below that of the atmosphere, thus confirming that law for pressures up to two atmospheres, as is seen from the following comparison, in which the experimental numbers are reduced to the standard of 100 at atmospheric pressure:—

Pressure.	Illuminating power.	
	Observed.	Calculated.
1 Atmosphere	100·	100
2 Atmospheres first ..	263·7	253
2 Atmospheres second ..	261·3	253

Further determinations, in which the illuminating power at three and four atmospheres pressure was compared, yielded results differing widely from this law, and indicating a much more rapid increase of light; but as the liability to errors of observation increases greatly at these higher pressures, I place very little confidence in the numbers obtained, which I will nevertheless here briefly state in the same form as the last Table. In these experiments, the lamp was fed with a mixture of five parts of vinic alcohol and one part of amylic alcohol. The lamp when fed with

this mixture had no appreciable illuminating effect under ord inar atmospheric pressure.

Pressure.	Illuminating power.	
	Observed.	Calculated.
3 Atmospheres	406	406
4 Atmospheres	959	559

In endeavouring to trace the causes of this variation of luminosity, it will be convenient first to consider the general conditions upon which the light of flames depends. The luminosity of the flames generally used for artificial light emanates from two sources; viz., first, from the ignition of minute particles of carbon floating in the shell of flame; and secondly, from the incandescence of gaseous matters. The latter source of illumination probably does not usually furnish more than one per cent., of the total amount of light; consequently nearly the whole of the light given out by flames under ordinary circumstances is due, as Davy first pointed out*, to the ignition of solid carbonaceous matter. The light emitted by incandescent gaseous particles becomes, however, much more prominent at very low pressures; and, as this light is not materially influenced by pressure, it causes the deviation from the law of diminution of light, seen at the lower extremities of the lines A C and A D in Diagram No. 1. In order to gain a clear conception of the mechanism of a candle or gas-flame, we must picture to ourselves, first a core of gas or vapour containing hydrocarbons, and secondly a shell of ignited matter closely surrounded on its outside by atmospheric air. The uninterrupted supply of gas or vapour to the core forces the contents of the latter constantly through the ignited shell, at the inner wall of which those hydrocarbons, which cannot exist at a bright red heat, either

* Philosophical Transactions, 1817, p. 64.

undergo decomposition into light carburetted hydrogen and free carbon, or imperfect combustion into water, carbonic oxide, and free carbon, or finally perfect combustion into water and carbonic oxide, or even carbonic acid, without any separation of free carbon. The nature of the decomposition or combustion which these hydrocarbons undergo on coming in contact with the ignited shell, thus evidently depends upon the amount of oxygen which gains access to the interior of the shell; if that quantity be insufficient to convert the whole of the carbon of the hydrocarbons into carbonic oxide, the residue will be precipitated, and the flame will be a more or less luminous one; whilst if the amount of oxygen present be sufficient, after burning the hydrogen, to consume the whole of the carbon to carbonic acid, or even to carbonic oxide, no light will be produced from the incandescence of carbon particles.

Now it is well known that the light of any flame may be increased by increasing the number of carbon particles simultaneously floating in it, provided those particles are consumed before they leave the flame, and are not evolved as smoke. I have also elsewhere shown * that the light of gas-flames, and doubtless that of candles and oil also, greatly depends upon the heat of the flame, the rise in temperature caused by merely heating the air supplied to a gas-lamp, by the waste heat of the flame itself, being sufficient to increase the light to the extent of 67 per cent. without any increased consumption of gas. Such being the conditions necessary for the *increase of light*, it is scarcely necessary to add that the reversal of these conditions, viz., the decrease in the number of particles of carbon existing in the flame at a given time, imperfect combustion allowing the escape of unconsumed carbon, and decrease of temperature in the flame determine a *diminished luminosity*.

One of the first causes which naturally suggests itself to account for the diminution of light by decreased atmospheric pressure, is the diminished amount of oxygen in a given bulk of the supporting medium rendering combustion imperfect, and thus either causing particles of carbon to escape unconsumed, or determining their conversion into carbonic oxide instead of carbonic acid. The effect of the first would be to diminish the luminosity, whilst the second would have the effect of decreasing the light indirectly by diminishing the temperature of the flame. A careful inspec-

* Ure's Dictionary of Arts, Manufactures, and Mines, 1860, article "Coal-gas."

tion of a gas or candle-flame, burning in an atmosphere undergoing gradual rarefaction, does not afford the slightest evidence of smoke, or even of an increased tendency to throw off fuliginous matter; on the contrary, the tendency to smoke obviously diminishes as the rarefaction progresses; whilst, on the other hand, the fact that an increase of pressure beyond that of the atmosphere causes the most smokeless flames to become smoky, renders utterly untenable the assumption that the escape of unconsumed carbon is one of the causes of diminished luminosity in rarefied atmospheres. Whether or not there is imperfect combustion in the sense of an escape of carbonic oxide instead of carbonic acid from the flame, could not be thus decided, and demanded a closer investigation.

To determine this point, I collected samples of the gases escaping from the chimney of the experimental flame (which in this was that of a sperm candle) when burning under atmospheric pressure, and again when burning under a pressure of only 8 inches of mercury. These gases were first treated with caustic potash to absorb carbonic acid; they were then exploded with an equal volume of electrolytic water-gas, and subsequently with excess of hydrogen. The explosion with water-gas caused no contraction, proving the absence of carbonic oxide. The numbers obtained give the following percentage composition of the two samples of gas :—

	Candle burning at atmospheric pressure	Candle burning under 8 inches mercurial pressure.
Nitrogen . .	81·28	81·58
Oxygen . .	11·73	10·30
Carbonic acid .	6·99	8·12
Carbonic oxide .	0·00	0·00
	100·00	100·00

These results prove that in both cases there was no escape of unconsumed combustible gas; consequently *the diminution of light in rarefied atmospheres is not due to imperfect combustion in any form.*

Taken in connexion with the experiments in compressed air, in which imperfect combustion attended with the evolution of fuliginous matter was very marked, these data lead to the remarkable conclusion that *the compression of air renders the*

combustion of gaseous matter less perfect; and that within certain limits at least, *the more rarefied the atmosphere in which flame burns, the more complete is its combustion.* Thus it is evident, not only that no diminution of light can arise from imperfect combustion in rarefied atmospheres, but also that no reduction of temperature in the flame can occur from the same cause.

A second cause of the diminution of the light of combustion in rarefied atmospheres, and its increase in compressed ones, might be sought for in a possible difference between the temperatures of the flame in the two cases. It is well known that if air be allowed to escape from a vessel into a vacuum, a considerable diminution of temperature ensues in the vessel from which the air escapes; and inasmuch, as the gaseous products of combustion assume a larger volume in rarefied atmospheres than in compressed ones, it can scarcely be doubted that the pyrometric thermal effect of a flame must be diminished to some extent by rarefying the medium in which it burns; nevertheless this effect may be nearly or quite neutralized by the smaller amount of refrigeration caused by the rarefied atmosphere. In order to elucidate this point, a spiral of platinum wire was ignited to visible redness in a flame of hydrogen; on then rarefying the air around the flame and wire, no appreciable alteration in the temperature of the platinum spiral could be noticed. A similar experiment was tried with an alcohol flame, and with the same result. A spiral of platinum wire placed under the receiver of an air-pump, was ignited to visible redness by a voltaic current; on exhausting the receiver, the glow of the platinum gradually increased nearly to whiteness. On readmitting the air, it again diminished to dull redness, showing that the refrigerating effect of rarefied air is much less than that of air at the ordinary pressure. Thus, whilst the temperature produced within a given flame is lowered by rarefaction, the escape of heat from its exterior is hindered by the same process,—the result apparently being that the actual temperature of the flame undergoes but little alteration. This confirms Davy's conclusion, that *rarefaction and compression, within certain limits at least, do not exert any considerable influence upon the heat of flame.*

Although an inquiry into two of the possible causes of the diminution of the light of combustion in rarefied atmospheres has thus failed to afford any explanation of the phenomenon, yet one of them indirectly points to what I believe to be the conditions determinating the variation in illuminating power. If it be true

that combustion is more complete in rare atmospheres than in dense ones, it follows that the light of a smokeless flame must decrease with a dimunition of pressure, since, with more perfect combustion, that is, with freer access of oxygen to every part of the flame, there must be a diminution of unconsumed carbon separated within the flame, and consequently a diminished amount of light evolved. In fact, the appearance of the experimental flame during the progress of rarefaction on the one hand, and of compression on the other, can scarcely leave a doubt on the mind of an observer, that the variation of luminosity depends essentially upon the admission of oxygen to that portion of the shell of flame where particles of carbon are usually precipitated, and where consequently the region of luminosity is situated. That an admission of oxygen or air to the interior of a luminous flame has the effect of greatly diminishing or even practically annihilating its luminosity, has been long known and even utilized in the wire-gauze and Bunsen's burners, where heat and not light is the object of the combustion of gas. But, it may be asked, what conditions are there in the combustion of flame in rarefied air that favour the admission of a larger proportion than usual of air to the interior of the flame? In reply, it may be stated that there are two conditions in such combustion, both of which directly tend to produce this result. The first of these conditions, and the one to which I conceive nearly the whole of the effect to be due, is the greater mobility of *rarefied* gaseous bodies, which must produce a more rapid admixture of the flame, gases, and external air than would otherwise take place. The second condition is the gradual, though slow, increase in the volume of the flame as the atmospheric pressure decreases, thus causing the flame to present a gradually increasing surface of contact with the exterior air. This alteration in the volume of flame by diminished pressure is more strikingly seen with a sperm candle than with gas. When such a candle burns under a pressure of two atmospheres, its flame presents the appearance of a sharp spike scarcely one-fourth of an inch in diameter at its lower and broadest part, the apex being lost in the dense smoke which issues from the upper portion of the flame. If the pressure be now diminished, the diameter of the spike markedly increases, especially about its centre, until at one-atmosphere pressure the flame assumes its ordinary appearance. On now rarefying the air, the transverse diameter of the flame goes on increasing until, when the pressure is reduced to about 6

mercurial inches, the flame becomes nearly globular with a diameter of about three-fourths of an inch.

Now, as the amount of combustible matter in the flame was maintained constant in the photometrical experiments detailed above, it follows that the increased external flame surface must so alter the conditions of combustion, as to bring the constant amount of combustible matter into contact with a gradually, increasing quantity of oxygen. That a large amount of air does, even under ordinary circumstances, gain access to the interior of gas and candle-flames, has been proved by the interesting researches upon the gases of these flames recently made by Hilgard,* who found 64 per cent. of nitrogen in the interior of a candle-flame, and by Landolt,† who detected 66 per cent. of nitrogen in the interior of a gas-flame; on no occasion, however, did these experimenters find oxygen in the luminous portion of the flame, although it was found in the blue or non-luminous section. I conceive, therefore, that these consequences of diminished pressure, viz., increased gaseous mobility and augmented volume of flame, are quite competent to explain the variations in luminosity resulting from alterations in the pressure of the supporting medium, and that *these variations in illuminating power depend chiefly, if not entirely, upon the ready access or comparative exclusion of atmospheric oxygen as regards the interior of the flame.*

In conclusion, the influence of atmospheric pressure upon the phenomena of combustion may be thus summed up:

1. The rate of burning of candles and other similar combustibles, whose flames depend upon the volatilization and ignition of combustible matter in contact with atmospheric air, is not perceptibly affected by the pressure of the supporting medium.

2. The rate of burning of self-supporting combustibles, like time-fuses, depends upon the rapidity of fusion of the combustible composition, which rapidity of fusion is diminished by the more rapid removal of the heated gases from the surface of the composition. Hence the rate of burning of combustibles of this class depends upon the pressure of the medium in which they are consumed. In the case of time-fuses, the increments in the time of burning are proportional to the decrements in the pressure of the surrounding medium.

3. The luminosity of ordinary flames depends upon the pressure of the supporting medium; and, between certain limits, the dimi-

* Ann. Ch. Pharm. xcii. 129. † Pogg. Ann., cxix. 389.

nution in illuminating power is directly proportional to the diminution in atmospheric pressure.

4. The variation in the illuminating power of flame by alterations in the pressure of the supporting medium depends chiefly, if not entirely, upon the ready access of atmospheric oxygen to, or its comparative exclusion from, the interior of the flame.

5. Down to a certain minimum limit, the more rarefied the atmosphere in which flame burns, the more perfect is its combustion.

XXXII.—*On the action of Carbonate of Ammonium on Magnesian Salts.*

By Edward Divers, M.D.

In all works on chemistry—especially analytical—it is stated, I believe, without exception, that carbonate of ammonium precipitates magnesian salts only very imperfectly, or not at all; and that salts of ammonium, when present in excess, entirely prevent this precipitation.* The object of the present paper is to show the singular incorrectness of this statement—since the precipitation is nearly complete—and to give some particulars of the nature of the reaction and the circumstances favouring it.

If dilute solutions of sulphate of magnesium, chloride of ammonium, and carbonate of ammonium be mixed so as to have excess of ammoniacal salt, especially the carbonate, no immediate effect will follow; but by allowing the mixture to stand, formation of a granular crystalline precipitate will always take place in ten minutes or so, if there is a large excess of carbonate of ammonium, in longer time if the excess be less.

Some of the precipitate, washed on a funnel with a dilute solution of carbonate of ammonium, and afterwards with a little water, yielded after ignition 15·86 p. c. of magnesia as the mean of three experiments (I. = 15·80; II. = 15·93; III. = 15·84).

* H. Rose, speaking of the precipitation of magnesia by phosphate of sodium from ammoniacal solutions, says that the solution must be rendered alkaline by caustic ammonia, not by carbonate of ammonium, as in the latter case, a certain quantity of ammonia-magnesian carbonate is always precipitated together with the phosphate. (*Traité complet de Chimie Analytique*, Paris, 1861, II, 46.)—Ed.

The double carbonate of magnesium and ammonium

$$Mg(NH_4), CO_3 . 2H_2O,$$

containing 15·87 p. c. magnesia, is therefore indicated.*

The following experiments were made to determine the circumstances favouring the precipitation of this salt:

I. Solutions of sulphate of magnesium containing one-tenth of salt, and of commercial carbonate of ammonium and caustic ammonia, made so as to contain as nearly as possible one-seventh of neutral carbonate, were mixed in various proportions, when it was found that simple carbonate of magnesium precipitated unless there were present 4 eq. of carbonate of ammonium to 1 eq. of sulphate of magnesium. When such a mixture was made, a semi-opaque crystalline deposit began to form after a few minutes, on the walls of the vessel, and rapidly increased. Next day the ammoniacal mother-liquor gave *no immediate precipitate* with phosphate of sodium, although a slight one gradually appeared.

II. One equivalent of sulphate of magnesium, it is evident, requires theoretically two equivalents of carbonate of ammonium for its conversion into double carbonate.

Solutions of sulphate of magnesium and of carbonate of ammonium, of the strength used in (I.), were mixed in the proportion of one equivalent of the former to two of the latter, after first adding to one of them different proportions of chloride of ammonium solution containing one-eighth of salt. In these experiments, it was found that nearly one equivalent of chloride of ammonium to one of sulphate of magnesium was required to prevent the precipitation of any simple carbonate of magnesium. In about a quarter of an hour, precipitation of double carbonate set in, which, compared with that in presence of excess of carbonate of ammonium, formed more slowly, gave a more transparent product, and after standing twenty-four hours, was less complete, phosphate of sodium giving an immediate and decided precipitate with the mother-liquor. When four equivalents of chloride of ammonium were added to one of sulphate of magnesium, the results were the same, and precipitation always occurred in presence of any quantity of ammoniacal salt that could at all come within the accepted meaning of the word "excess."

III. The same mixture was made as in (I.), but in addition to the four equivalents of carbonate, 1 eq. of chloride of ammonium was added. The result was the same as that of (I.), except that the precipitation of the magnesia as double carbonate seemed to

* See Gmelin's Handbook III, 244.

be even more complete: for next day phosphate of sodium yielded but a mere trace of precipitate with the mother-liquor.

IV. The next experiments had for their object the investigation of the effects of quantities of carbonate of ammonium insufficient for the conversion of all the sulphate of magnesium into double carbonate. The carbonate of ammonium was added to a mixture of equivaleut proportions of sulphate of magnesium and chloride of ammonium. In these cases, no precipitate appeared till next day or even later, but it did eventually appear, even if only a trace of carbonate was added, so as merely to give a faint ammoniacal odour to the solution, taking the precaution to close the vessel to prevent volatilization of the ammonia.

V. Having mixed the solutions in the proportions of one equivalent of sulphate of magnesium, two of chloride of ammonium, and four of carbonate, portions of the mixture were taken before precipitation had commenced, and diluted until there was in five separate experiments one of magnesia in one, two, three, four, and five-thousand parts respectively. No precipitates formed in any after standing for days. But, at the time of making up these solutions, some of each was mixed with more solution of carbonate of ammonium, so as to be rendered strongly ammoniacal, and in all these precipitation occurred after from 24 hours to 3 or 4 days; and this, not in order of their strength in magnesia, but of their strength in carbonate of ammonium, so that the weakest solution, which now contained less than one five-thousandth of magnesia, was one of the first to precipitate, happening to have been somewhat more freely mixed with carbonate of ammonium than the others.

VI. The solubility of the double salt was tried in the following liquids:—Water, and solutions of chloride, carbonate, and bicarbonate of ammonium.

1. In water.—Guibourt states that the double carbonate of magnesium and ammonium is soluble in this medium. Bucholz, on the other hand, says that it decomposes into a soluble double salt containing excess of carbonate of ammonium and an insoluble salt containing excess of magnesian carbonate.

The statement of Bucholz appears to be a mistake, and that of Guibourt must be considered imperfect: for the action of water is as follows.—If the salt be treated with water on a filter, some of it dissolves and some decomposes into its constituent carbonates, so that the filtrate contains double carbonate of magnesium and ammonium together with free carbonate of ammonium, while that

which remains on the filter (after washing until magnesia ceases to appear in the filtrate—an operation soon terminated) is found to be carbonate of magnesium only: for when treated with fixed alkali, it yields no ammonia. But if, to a beaker of water, the finely powdered salt be added in small quantities at a time and stirred, it will dissolve perfectly to a considerable extent. When, however, an excess of the salt is added, it is rapidly attacked by the water, which dissolves out the carbonate of ammonium, leaving the carbonate of magnesium in a compact crystalline mass; and not only does this decomposition take place, but the free carbonate of ammonium thus thrown into the solution seems to induce the decomposition of the double carbonate already dissolved: for precipitation of crystalline carbonate of magnesium soon sets in. (This secondary decomposition may be due to the presence of carbonate of magnesium in the free state, instead of that carbonate of ammonium.) But if, as soon as the water ceases to dissolve more of the salt, it be filtered from the excess, a considerable quantity of clear solution passes through before decomposition commences in the remainder. If then any further quantity of the filtrate be prevented entering into that already obtained, the solution will remain clear for a while, after which it will decompose into the separate carbonates. Dilution with water greatly retards this decomposition.

Some of the filtered solution, as completely saturated as could be without decomposition immediately ensuing, was precipitated with phosphate of sodium. 113·66 grms. were thus found to contain 1·5975 grms. of double salt. One part was therefore dissolved in 71·15 of water. The solution gave an immediate gelatinous precipitate (of magnesia) with ammonia.

Some of the same clear solution was left for twenty-four hours, and the crystalline precipitate which had formed, was collected, washed with a very little water, pressed between folds of bibulous paper, and dried. It gave off no ammonia on treatment with potassa. By ignition, 0·82 grm. left 0·244 grm. of magnesia = 29·76 p.c. The neutral carbonate of magnesium with three of water of crystallization contains 29 p. c. of magnesia.

2. In chloride of ammonium solution. In this the double carbonate dissolves sufficiently to yield an immediate, though slight, precipitate with phosphate of sodium. The solution had an ammoniacal odour (the dry double salt has none). *Carbonate of ammonium caused a precipitate in a few minutes in the solution.*

3. In solution of carbonate of ammonium, the double salt

appears almost insoluble. The filtered solution gave a slight precipitate with phosphate of sodium only after a few minutes.

It would seem that the double carbonate is in some way decomposed to a small extent by solutions of carbonate of ammonium, even the strongest. For when the powdered salt has settled down, there remains suspended for some time a slight milkiness, a result which does not occur with water or chloride of ammonium.

Solutions of bicarbonate of ammonium act just as those of the carbonate.

4. The mother-liquor of a solution which had deposited the double salt and contained an access of carbonate of ammonium and a large excess of chloride and sulphate of ammonium, was found to contain one part of magnesia in about 4660 pts. of solution. Ex. V shows that the precipitation would have been much more complete had there been a *large* excess of carbonate of ammonium. Still the result is worth recording, as furnishing an additional illustration of the insufficiency of ammoniacal salt to prevent precipitation of magnesia by carbonate of ammonium.

From the above experiments it seems to be shown—

1. That, contrary to general statements, carbonate of ammonium *does* precipitate magnesian salts in presence of excess of ammoniacal salts.

2. That the precipitate then formed is the double carbonate of magnesium and ammonium.

3. That this salt is soluble to some extent in water, but very slightly so in solutions of chloride and sulphate of ammonium, almost totally insoluble in that of carbonate of ammonium; and that, within certain wide limits, the double salt is less soluble, according to the strength of the liquid, in salts of ammonium, particularly the carbonate.

Besides the analytical bearings of these results, they are also of interest as furnishing us with a cheap and ready mode of preparing the double carbonate of magnesium and ammonium, which it is believed, will be particularly useful in medicine; it also readily yields a neutral carbonate of magnesium, either by the action of water or by a heat not greater than 100° C. This precipitation of the double carbonate may possibly supply the manufacturer with a mode of separating magnesia from its solutions.

The double carbonate of zinc and ammonium does not seem to be formed by a similar method.